SYNTHESIS AND LUMINESCENT PROPERTIES OF BIMETALLIC GOLD(I) AND SILVER(I) PYRAZOLATE COMPLEXES

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This work is dedicated to my beloved parent, Sabran and Sa'adiah, and my siblings, who are always been there for me, and have never doubted my dreams, and also to all my friends, who has shared to joyful tears and get through the hard time together.

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ABSTRACT

Luminescent d^{10} complexes of gold(I) and silver(I) have particularly received much attention due to their phosphorescent characteristics originating from metal–metal interactions and their applications in organic light–emitting diodes, sensors, catalysis, optics, and photonics. While bimetallic gold(I) and silver(I) complexes have been synthesized as clusters or mixed–compounds, luminescent studies of molecular self–assembly of bimetallic gold(I) and silver(I) complexes have not yet been reported. Therefore, this research aimed to study the phosphorescent properties of molecularly self–assembled trinuclear bimetallic gold(I) and silver(I) pyrazolate complexes (**4**[Au_3Pz_3]@[Ag_3Pz_3]R) using fluorescence spectroscopy. Both trinuclear gold(I) and silver(I) pyrazolate complexes, **2**[Au_3Pz_3]R and **3**[Ag_3Pz_3]R were successfully synthesized from pyrazole ligands having different alkyl chains (**1**(PzH)R; R = H, $(OCH_3)_2$Bn, $(OC_{10}TEG)_3$Bn) with chloro(dimethylsulfide) gold(I) ([$Au(SMe_2)$]Cl) and silver(I) hexafluorophosphate ($AgPF_6$). Bimetallic pyrazolate complexes **4**[Au_3Pz_3]@[Ag_3Pz_3]R were synthesized by stirring a mixture of **2**[Au_3Pz_3]R and **3**[Ag_3Pz_3]R in dry dichloromethane for 1 hour with molar ratios of **2**[Au_3Pz_3]R to **3**[Ag_3Pz_3]R of 1:1, 1:2, 1:3, 1:5, 1:10, 2:1, 3:1, and 5:1, whereas molar ratios of 1:1, 1:2, and 2:1 were used for synthesis of $(OC_{10}TEG)_3$Bn. At molar ratio of 1:1, the fluorescence spectrum of the resulting complex exhibited only one emission peak centered at 633 nm compared to 691 nm for **2**[Au_3Pz_3]H and 471 nm for **3**[Ag_3Pz_3]H when excited at 280 nm. Based on the luminescent changes at molar ratio 1:1, it is proposed that the formed bimetallic complex might be the gold(I)–silver(I) cluster, **4**[Au_3Pz_3]@[Ag_3Pz_3]H. On the other hand, the bimetallic pyrazolate complex obtained at molar ratio 1:1 was **4**[Au_3Pz_3]@[Ag_3Pz_3]$(OCH_3)_2$Bn when the alkyl chain was changed by $(OCH_3)_2$Bn. Two emission peaks at 463 and 606 nm were shown in fluorescence spectra where the intensity of the peak at 463 nm assigned to gold(I)–silver(I) interactions is relatively much lower in comparison to the peak at 606 nm of gold(I)–gold(I) interaction. The result obviously suggests molecular structural changes which may be associated to increase rigidity of side chain of the bimetallic complexes. When the alkyl chain was changed by $(OC_{10}TEG)_3$Bn, the resulting bimetallic amphiphilic complex, **4**[Au_3Pz_3]@[Ag_3Pz_3]$(OC_{10}TEG)_3$Bn with molar ratio 1:1 exhibited two emission peaks at 491 and 710 nm with almost the same intensity upon excitation at 276 nm, while **2**[Au_3Pz_3]$(OC_{10}TEG)_3$Bn and **3**[Ag_3Pz_3]$(OC_{10}TEG)_3$Bn showed emission peaks at 699 nm and 537 nm, corresponding to gold(I) and silver(I), respectively. These findings suggested the formation of bimetallic amphiphilic complex *via* self–assembly of alternating gold(I) and silver(I) complexes due to the more flexible amphiphilic alkyl chains. Of significance, the characteristic luminescent properties of **4**[Au_3Pz_3]@[Ag_3Pz_3]R with different types of pyrazole ligands and molar ratios could be ascribed to changes of the gold(I)–silver(I) coordination in the self–assembled structures.

ABSTRAK

Kompleks pendarcahaya d^{10} aurum(I) dan argentum(I) telah menjadi tumpuan utama kerana ciri pendarfosfornya yang berpunca daripada interaksi antara logam–logam dan penggunaannya dalam diod pemancar cahaya organik, sensor, pemangkinan, optik dan fotonik. Walaupun kompleks dwilogam aurum(I) dan argentum(I) telah disintesis sebagai gugusan atau sebatian campuran, kajian pendarcahaya bagi molekul swahimpun kompleks dwilogam aurum(I) dan argentum(I) masih belum dilaporkan. Oleh itu, penyelidikan ini bertujuan untuk mengkaji ciri pendarfosfor molekul swahimpun kompleks trinuklear dwilogam aurum(I) dan argentum(I) pirazolat (**4**$[Au_3Pz_3]$@$[Ag_3Pz_3]$R) menggunakan spektroskopi fotopendarcahaya. Kedua–dua kompleks trinuklear aurum(I) dan argentum(I) pirazolat (**2**$[Au_3Pz_3]$R dan **3**$[Ag_3Pz_3]$R) telah berjaya disintesis daripada ligan pirazola yang mempunyai rantai alkil yang berbeza (R = H, $(OCH_3)_2$Bn, $(OC_{10}TEG)_3$Bn) dengan aurum(I) kloro(dimetilsulfida) ($[Au(SMe_2)]Cl$) dan argentum(I) heksafluorofosfat ($AgPF_6$). Kompleks dwilogam pirazolat **4**$[Au_3Pz_3]$@$[Ag_3Pz_3]$R telah disintesis dengan mencampurkan **2**$[Au_3Pz_3]$R dan **3**$[Ag_3Pz_3]$R dalam diklorometana kering selama satu jam dengan nisbah molar 1:1, 1:2, 1:3, 1:5, 1:10, 2:1, 3:1, dan 5:1, manakala nisbah molar 1:1, 1:2, dan 2:1 telah digunakan untuk sintesis $(OC_{10}TEG)_3$Bn. Pada nisbah molar 1:1, spektrum pendarfluor kompleks dwilogam yang terhasil mempamerkan satu puncak pancaran yang berpusat pada sekitar 633 nm berbanding 691 nm bagi **2**$[Au_3Pz_3]$H dan 471 nm bagi **3**$[Ag_3Pz_3]$H apabila diuja pada 280 nm. Berdasarkan perubahan pendarfluor pada nisbah molar 1:1, adalah dicadangkan kompleks dwilogam yang terbentuk berkemungkinan adalah gugusan aurum(I)–argentum(I), **4**$[Au_3Pz_3]$@$[Ag_3Pz_3]$H. Sebaliknya, komplek dwilogam pirazolat yang diperolehi pada nisbah molar 1:1 adalah **4**$[Au_3Pz_3]$@$[Ag_3Pz_3](OCH_3)_2$Bn apabila rantai alkil digantikan dengan $(OCH_3)_2$Bn. Dua puncak pancaran pada 463 dan 606 nm kelihatan dalam spektrum pendarfluor dengan keamatan puncak pada 463 nm yang dipadankan kepada interaksi aurum(I)–argentum(I) secara relatif lebih rendah berbanding keamatan puncak pada 606 nm hasil interaksi aurum(I)–aurum(I). Keputusan ini jelas mencadangkan perubahan struktur molekul mungkin disebabkan oleh peningkatan ketegaran rantai sisi kompleks dwilogam tersebut. Apabila rantai alkil digantikan dengan $(OC_{10}TEG)_3$Bn, komplek amfifilik yang terhasil, **4**$[Au_3Pz_3]$@$[Ag_3Pz_3](OC_{10}TEG)_3$Bn pada nisbah molar 1:1 menunjukkan dua jalur pancaran pada 491 dan 710 nm dengan keamatan puncak yang hampir sama apabila diuja pada 276 nm, manakala **2**$[Au_3Pz_3](OC_{10}TEG)_3$Bn dan **3**$[Ag_3Pz_3](OC_{10}TEG)_3$Bn menunjukkan jalur pancaran pada 699 and 537 nm, masing–masing sepadan dengan aurum(I) dan argentum(I). Keputusan ini mencadangkan pembentukan kompleks dwilogam amfifilik melalui penswahimpunan kompleks aurum(I) dan argentum(I) secara berselang–seli disebabkan rantai alkil amfifilik yang lebih fleksibel. Yang lebih penting, sifat ciri pendarcahaya **4**$[Au_3Pz_3]$@$[Ag_3Pz_3]$R dengan jenis ligan pirazola dan nisbah molar yang berbeza boleh dianggap berpunca daripada perubahan pengkoordinatan aurum(I)–argentum(I) dalam struktur swahimpun tersebut.

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MOFs	-	Metal Organic Frameworks
LF	-	Ligand Field
MLCT	-	Metal–to–Ligand Charge Transfer
IL	-	Intraligand
MC	-	Metal Centered
LMCT	-	Ligand–to–Metal Charge Transfer
LMMCT	-	Ligand–to–Metal–to–Metal Charge Transfer
VOCs	-	Volatile Organic Compounds
NLO	-	Non–linear Optic
OLEDs	-	Organic Light–Emitting Devices
PL	-	Photoluminescence
DNT	-	2,4–Dinitrotoluene
DMNB	-	2,3–Dimethyl–2,3–Dinitrobutane
UV	-	Ultra Violet
DCM	-	Dichloromethane
1*BnBr	-	Benzyl Bromide
1**BnAcac	-	Benzyl Acetyl Acetonate
1(PzH)R	-	Pyrazole Ligands
2[Au_3Pz_3]R	-	Trinuclear Gold(I) Pyrazolate Complexes
3[Ag_3Pz_3]R	-	Trinuclear Silver(I) Pyrazolate Complexes
4[Au_3Pz_3]@[Ag_3Pz_3]R	-	Bimetallic Trinuclear Gold(I) and Silver(I) Pyrazolate Complexes
^{1}H–NMR	-	Proton Nuclear Magnetic Resonance
^{13}C–NMR	-	Carbon Nuclear Magnetic Resonance
FT–IR	-	Fourier Transform Infrared Spectroscopy
XRD	-	X–ray diffractometer

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Luminescent materials are well–known as materials having phosphors or compounds that give emission properties when they absorb energy from light [1]. Since last few decades, many researchers have paid attention to develop the next generation of high performance luminescent materials in display, lighting, optical devices, sensing, and imaging [1–4]. However, some limitations on their physical properties such as quantum yield, spectral energy distribution, life time, and emission as well as their chemical stability and composition [1, 3] have been generally found as a parameter for reducing their performance.

Recently, researchers have been focused on development of new materials having high luminescent properties not only from organic or inorganic but also from both organic and inorganic phosphor compounds. Thereby, the development will potentially provide new functional luminescent materials such as metal organic phosphors [5], doped zeolites [6], metal organic frameworks (MOFs) [7], and composites [8]. For example, Lee *et al.* have reported that new blue emitting phosphor of $Na_xCa_{1-x}Al_{2-x}Si_{2+x}O_8:Eu^{2+}$ ($NCASO:Eu^{2+}$) with excitation wavelength at wide spectral range from 250 to 420 nm [5] have been used as light emitting materials. Moreover, modification of Europium ion (Eu^{3+})–exchanged zeolite L with silylated β–diketone was reported to have a strong red emission due to an energy transfer of grafted molecules to the Eu^{3+} ions [6]. Recently, Cui *et al.* [7] have

reported that mix lanthanide ions with MOF showed two emission spectra at wide range temperature and were potentially used as a thermometer. In addition, composite luminescent materials containing of 5,10,15,20–tetrakis(2,3,4,5,6–pentafluorophenyl) porphyrin and tris(phenanthroline) with palladium(II) and ruthenium(I) as a metal ion (Pd–TFFP and Ru–phen) as reported previously in 2006 by Borisov and his co–workers can be used as dual oxygen and temperature sensor simultaneously [8].

Luminescent materials containing of metal organic complexes or known as organometallic have received great interest in recent years after the first report on photophysical and photochemical behaviors of ruthenium(II) bipyridine complexes by Adamson and Demas in 1971 [9]. Since this finding, numerous studies have been further developed and explored to significantly improve the performance. In 2001, Che and his co–workers have found that zinc(II) complex containing naphthyridyl ligand can give luminescent properties both in solution as an blue emission and in solid state as a white emission [10]. In some cases, transition metal complexes were getting more attention due to the capability to exhibit phosphorescent properties originating from triplet excited state of metal–to–ligand charge transfer (MLCT) [11–16]. For example, terpyridine ligand upon complexation with platinum ($[Pt(terpy)Cl]^{+}$) was reported to form luminescence properties in both solid state and glass by Bailey and his group at 1995 [15]. However, the complexes were found to be non–emissive in the solution state due to a low energy of ligand field (LF) excited state from d–d transition.

Apart of monometallic complexes, some studies have highlighted that bimetallic or heterometallic complexes can be potentially used as optical devices [16], catalysts [17], and sensors [18]. Recently in 2013, cyclometalated d^8 platinum(II) complexes have been reported to self–assembly via both a weak non–covalent π–π and Pt–Pt interactions that are potentially used as organic light–emitting devices [19]. On following year, Li *et al.* was reported that bimetallic binuclear nickel and cobalt complexes of bis(benzotriazole iminophenolate) were highly reactive as a catalyst for copolymerization of cyclohexene oxide and carbon dioxide [17].

While most of studies were focused on d^6 and d^8 metal complexes, unique spectroscopy features of d^{10} metal complexes in their absorption and emission properties have been investigated based on a weak non–covalent bonding of metal–metal (metallophilic) interactions [20]. Recently, development on d^{10} metal complexes are not only from platinum group but also involving zinc(II), cadmium(II),gold(I), silver(I), and copper(I) complexes which are more considerable [21–24]. Peculiarly, gold(I), silver(I), and copper(I) complexes have received huge attention due to their characteristics of phosphorescent properties [25–32]. Gold(I), silver(I), and copper(I) pyrazolate complexes having different type of alkyl chains have been reported to self–assemble via weak metal–metal interactions [20] to form "chair like" coordination geometry of a cylindrical structure [29] and having high luminescent properties. In addition, Omary *et al.* have reported that dinuclear and mononuclear copper(I) and silver(I) complexes of 3,5–bis(triflouromethyl)pyrazole ligand gave blue emission with short lifetimes [28]. Subsequently in 2005, this group has also reported to form supramolecular structure with luminescent changes upon complexation pyrazole ligands with gold(I), silver(I), and copper(I)metal ions [29]. Since these metal complexes have been reported to give high luminescent properties, it is interesting to investigate their potential applications such as vapochromic sensors where in 2011, trinuclear silver(I) pyrazolate complex was reported as a vapochromic selective sensor to benzene by Rawashdeh–Omary [32].

Instead of focusing on single metal complexes, some researchers also interested to study on the luminescence properties of bimetallic d^{10} complexes since these complexes showed great potential in various applications [33–35]. In 2004, heterometallic gold(I)–thallium(I) (Au–Tl) complex was reported as a vapochromic sensor due to its' photophysical properties by Fernandez *et al.* [34]. On the other hands, Pina and his co–workers were reported that bimetallic gold–copper (Au–Cu) complex potentially can be used as a catalyst for oxidation of benzyl alcohol to benzaldehyde [35]. Nowadays, heterometallic gold–silver complexes have received much attention due to their photophysical and photochemical properties [36–43]. Pioneering of Omary and co–workers [36] and Burini and Fackler group [33, 37], the development of polymeric materials based on heterometallic gold–silver complexes

have been increased extensively [38] and showed potential applications in sensors [39], catalysts [40, 41], optics, and photonics [42]. For example, dimers of gold(I)–silver(I) mixed–metal complexes from gold(I) carbeniates, gold(I) benzylimidazolates, and silver(I) 3,5–diphenylpyrazolates were successfully synthesized by varying the molar ratios and found to be excellent candidate as a catalyst [40, 41].

Since investigation of bimetallic gold(I)–silver(I) complexes have been found to give excellent phosphorescent properties in the single crystals form [40], a lot of researches have been done to study their photochemical and photophysical properties. Recently in 2012, polynuclear organometallic of gold(I)–gold(I), gold(I)–silver(I), and gold(I)–copper(I) having bidentate ligands were reported to give high luminescent properties and can be used as active antimicrobial agents [44]. Although bimetallic gold(I)–silver(I) complexes have been synthesized in single crystals as a cluster or mix compounds, no example of luminescent studies for molecular assembly of bimetallic gold(I)–silver(I) complexes with various of alkyl side chains has yet been reported. Therefore, it would be a big challenge to study the phosphorescent properties of molecular assembled trinuclear bimetallic gold(I)–silver(I) pyrazolate complexes having different kinds of alkyl side chains and variation of the molar ratios by using photoluminescent spectroscopy. It is expected that the molar ratios of these bimetallic complexes will not only affect on the molecular structure of complexes but also posses' unique phosphorescent properties.

1.2 Problem Statement

In 2003, Yang and Raptis have reported that trimeric gold(I) pyrazolate complex can self–assembly via gold–gold (aurophilic) interactions to show a red emission when excited at 230 nm [27]. On the other hands, the luminescent properties of trinuclear pyrazolate gold(I), silver(I), and copper(I) complexes have been further studied to investigate effect of the different metals on their supramolecular structure and as well as luminescent properties [29]. Since

developments on luminescent properties of single metal complexes have showed great potential in many applications, a few researches have also been done to study unique properties of bimetallic complexes.

Considering bimetallic gold–silver complexes have been found to give characteristic photophysical and photochemical properties for vapochromic sensors of volatile organic compounds (VOCs) [39], non–linear optic (NLO) materials [42], and organic light–emitting devices (OLEDs), it is an interesting challenge to synthesize molecular assembly of bimetallic gold(I)–silver(I) pyrazolate complexes having different kinds of alkyl side chains. However, no examples of self–assembled trinuclear bimetallic gold(I)–silver(I) pyrazolate complexes have been found to give phosphorescent properties with control of alkyl side chains. Thus, the goal of this research is to vary the molar ratios of mixed trinuclear gold(I) pyrazolate complex ($[Au_3Pz_3]$) and trinuclear silver(I) pyrazolate complex ($[Ag_3Pz_3]$) and then study the effect of the molar ratios on the luminescent properties. Finally, the resulting molecular assembled trinuclear bimetallic gold(I) and silver(I) pyrazolate ($[Au_3Pz_3]@[Ag_3Pz_3]$) complexes are expected to give unique phosphorescent properties.

1.3 Objectives of the Study

The objectives of this research can be separated as below:

a) To synthesize pyrazole ligands with different alkyl side chains.
b) To synthesize trinuclear gold(I) and silver(I)pyrazolate complexes having different alkyl side chains.
c) To synthesize the trinuclear bimetallic gold(I) and silver(I) pyrazolate complexes by varying the molar ratios of gold(I)pyrazolate complex to silver(I)pyrazolate complex.
d) To investigate the luminescent properties of the resulting trinuclear bimetallic gold(I) and silver(I)pyrazolate complexes.

1.4 Scope of the Study

The trinuclear gold(I) and silver(I) pyrazolate complexes were synthesized by using different pyrazole ligands attached with various alkyl chains; H, $(OCH_3)_2Bn$, and $(OC_{10}TEG)_3Bn$. The trinuclear bimetallic gold(I) and silver(I) pyrazolate complexes were prepared by mixing the gold(I) and silver(I) pyrazolate complexes with different molar ratios from 1:10, 1:5, 1:3, 1:2, 1:1, 1:2, 1:3, and 1:5, except for $C_{10}TEG$ only using 1:2, 1:1, and 1:2.

The characterization of the resulting trinuclear gold(I), silver(I), and bimetallic gold(I) and silver(I) pyrazolate complexes was carried out by using Proton Nuclear Magnetic Resonance (^{1}H–NMR), Carbon Nuclear Magnetic Resonance (^{13}C–NMR), Fourier Transform Infrared Spectroscopy (FT–IR), Ultraviolet Spectroscopy (UV), Matrix–assisted laser desorption/ionization time–of–flight mass spectrometry (MALDI–TOF–MS), and Liquid chromatography time–of–flight mass spectrometry (LC–TOF–MS). Structural analyses were confirmed by using X–Ray Diffraction (XRD), while the luminescent properties were studied by using spectroflourophotometer. Photograph was taken by using digital camera with the macro zoom under UV lamp in the dark room.

1.5 Significance of the Study

The significance of this research is control the luminescent properties of bimetallic gold(I) and silver(I) pyrazolate complexes by synthesizing different alkyl side chains attached to pyrazole ligands. The resulting bimetallic complexes are expected to give unique luminescent properties by changing the molar ratios of gold(I) pyrazolate complex to silver(I) pyrazolate complex from 1:10, 1:5, 1:3, 1:2, 1:1, 1:2, 1:3, and 1:5, except for $C_{10}TEG$ only using 1:2, 1:1, and 1:2. It is believed

that these bimetallic complexes with characteristics of luminescent properties can be used for potential applications in such as VOC sensors and NLO materials for imaging and optical data storage.

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